

Article

Heavy Liquid Separation Method for Enhancement of Trace Asbestos Detection

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Abstract: Powder X-ray diffraction (XRD) is a widely accepted technique for detecting trace asbestos content in solid samples. However, accurately quantifying asbestos concentrations below 0.5 wt% presents significant challenges with XRD alone. To address this limitation, we conducted a meticulous quantitative analysis using XRD on synthetic samples of talc-based powder spiked with varying amounts of natural tremolite and anthophyllite asbestos. At concentrations exceeding 0.5 wt%, both tremolite and anthophyllite displayed distinct XRD peaks. Yet, at lower concentrations (0.1 wt% and 0.05 wt%), the diffraction peaks of the contaminants became less prominent. To improve detection sensitivity, we explored different protocols of heavy liquid separation utilizing sodium polytungstate (SPT) to concentrate asbestos relative to the other mineral components. The optimized protocol, employing SPT with a density of 2.89 g/cm³, effectively separated amphibole asbestos from lighter, commonly associated minerals, like talc, clinocllore, and mica. Subsequent powder XRD analysis of the heavy fraction confirmed the successful removal of non-target materials, enhancing the diffraction peaks of tremolite and anthophyllite. Tremolite exhibited comparatively less weight loss than anthophyllite during this separation process. This study establishes the theoretical and practical viability of employing centrifugation in a heavy liquid to separate tremolite and anthophyllite from talc, providing valuable insights for asbestos detection and quantification in challenging scenarios.

Keywords: heavy liquid separation; powder X-ray diffraction; sodium polytungstate; tremolite; anthophyllite; talc-based powder



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1. Introduction

The presence of asbestos minerals in geological formations is often associated with processes such as metamorphism and hydrothermal activity [1,2]. Metamorphism entails changes in the composition and structure of pre-existing rocks due to factors such as heat, pressure, deformation, and fluid interactions. There are two primary types of metamorphism—contact and regional—which have also been linked to the formation of various commercially valuable materials. The term “asbestos” refers to a group of six naturally occurring minerals characterized by crystalline structures featuring slender, needle-like fibers that can easily become airborne when disturbed [3]. Geological variability influences the occurrence of asbestos, commonly found in serpentine or amphibole-rich formations. These fibers disperse through natural and industrial processes, appearing in the atmosphere, hydrosphere, and soil. Among the recognized asbestos minerals are tremolite and anthophyllite, both members of the amphibole mineral group. These minerals can exist in both fibrous and non-fibrous forms and often occur associated with commercial minerals, including talc for cosmetics [4–7] and vermiculite for agriculture [8–13].

Tremolite, Ca₂Mg₅Si₈O₂₂(OH)₂ is named after its discovery in the Tremola Valley, Switzerland. Part of the actinolite-ferroactinolite solid-solution series, tremolite's color

varies based on iron content, appearing colorless or white in its pure form. Specimens with higher iron concentrations display shades of gray, gray green, green, dark green, or nearly black. Prismatic or fibrous tremolite crystals range from short to long, commonly observed as unterminated bladed crystals, parallel aggregates, or radiating groups. Tremolite is frequently associated with minerals such as calcite, dolomite, garnet, wollastonite, talc, diopside, forsterite, cummingtonite, magnesio-cummingtonite, riebeckite, and winchite [2, 14–17].

Anthophyllite, named for its leaf-like appearance, with ideal chemical formula $Mg_7Si_8O_{22}(OH)_2$, displays clove-brown to dark-brown hues, pale green, gray, or white and is typically found in columnar-to-fibrous masses. It forms a Mg-Fe solid solution with ferro-anthophyllite, $Fe_7Si_8O_{22}(OH)_2$. The anthophyllite series is associated with minerals such as cordierite, talc, chlorite, sillimanite, mica, olivine, hornblende, gedrite, garnet, cummingtonite, staurolite, and plagioclase [2,14–16,18].

Talc and vermiculite, potential sources of asbestos fibers, undergo industrial processing for various applications. Stringent regulations and bans on asbestos mining and usage have been introduced globally due to documented health risks. Despite these restrictions, studying asbestos-like minerals such as tremolite and anthophyllite remains pertinent for specific industrial uses. Regulatory measures, particularly by the Food and Drug Administration, have limited asbestos in pharmaceutical talc and cosmetics. Asbestos, notorious for its health impacts, incurs substantial removal costs globally. Traditional analytical methods for asbestos detection have limitations, necessitating the development of advanced approaches for accurate quantification.

Accurately identifying and characterizing asbestos minerals consider grain morphology, chemical composition, and crystal structure. Various analytical methods are employed based on study objectives. Identification relies on understanding physical and chemical properties, with asbestos fibers possessing an aspect ratio greater than 3:1 [3,19]. Various techniques, such as polarized light microscopy (PLM) [20], phase contrast microscopy (PCM) [21], X-ray diffraction (XRD) [22,23], electron microscopy (SEM/TEM) [24,25], Raman spectroscopy [26], fluorescence microscopy [27], and thermal analysis [28–30], are utilized for detecting low levels of asbestos. It is crucial to recognize that each technique is subject to inherent limitations, emphasizing the need for a comprehensive approach and careful consideration of specific analysis requirements to ensure accurate results.

The Interagency Working Group on Asbestos in Consumer Products (IWGACP) recommends incorporating TEM analysis into all assessments for asbestos and other amphibole mineral particles in talc and talc-containing cosmetics, unless the sample has been rejected due to prior asbestos detection through XRD or PLM [31]. Light microscopy is a quick method for concentrations above 1%, while XRD serves as a screening method for detecting amphibole or serpentine asbestos. However, XRD has limited applicability for trace phases (<1 wt%) due to interference from other minerals. The nominal sensitivity of XRD for detecting amphibole in talc is 0.5% by weight [22,23].

Optimizing sample preparation techniques enhances the sensitivity of analytical methods, especially for detecting and quantifying trace phases. Methods of isolating and concentrating the analyte from complex matrices are crucial to achieving heightened sensitivity. Eliminating non-target materials, especially those interfering with the target analyte, becomes essential. The use of heavy liquid separation (HLS) for separating minerals with varying densities is a longstanding technique based on density differences. HLS is a fundamental technique taught in mineralogy, geology, and geological science courses worldwide. HLS solutions are readily available from chemical supply companies. While HLS is an established method for separating asbestos from vermiculite building materials [32], there are only a few published HLS methods specifically tailored for separating asbestos particles from talc [33,34]. Numerous researchers have contributed to the body of knowledge regarding acceptable methods for mineral separation using heavy liquids [35–37]. One example of HLS in action involved the separation of chrysotile from interfering minerals using a solution of 1,1,2,2-tetrabromoethane and carbon tetrachloride, followed by centrifugation. Asbestos fibers were then collected and identified using infrared spec-

tral analysis, demonstrating successful separation and concentration [38]. Another study utilized bromoform and tetrabromoethane for density-based separation of tremolite, cummingtonite, and grunerite from quartz, micas, and other silicates [39]. Although this study did not focus on asbestos in talc, its practical procedures for mineral separation could potentially be applied to asbestos-and-talc separation.

Asbestos fibers in the environment pose significant health risks due to their high biopersistence and association with carcinogenicity and pulmonary diseases [40–44]. To mitigate these risks, it is crucial to develop increasingly sensitive analytical methods capable of detecting and identifying trace concentrations of asbestos. This research aims to address this need by focusing on developing methods and protocols for effectively detecting small amounts of environmental asbestos. In addition, there is a strong motivation to improve the quantitative determination of asbestos concentrations through utilization of advanced analytical techniques, using powder XRD and heavy liquid separation and including electron microprobe analysis for chemical analysis. By advancing the capabilities of asbestos detection and quantification, this research seeks to contribute to the protection of human health and the environment.

2. Materials and Methods

2.1. Samples

In this study, we utilized natural tremolite and natural anthophyllite samples and talc-based powder. Talc-based powder is a cosmetic or personal care product that predominantly consists of talc as its primary ingredient. Talc, a naturally occurring mineral, is finely ground to create a powder with desirable properties, such as absorbency, smoothness, and a soft texture [5]. The fibrous tremolite found in McIlroy Mine in Inyo County, California, was primarily extracted and supplied to Powhatan Mining Company for utilization in crucible filters. Slip-fiber tremolite was found in a fault zone in limestone and dolomite [45,46]. It is known that these fibers have been used as reference standards by the Health and Safety Laboratory (UK) since 2000 and as standardized materials by the National Institute for Occupational Safety and Health (NIOSH) since 2014. The natural anthophyllite specimen was derived from a “Hermanov sphere”, a mineral aggregation originating from Heřmanov, Velke Mezirici, Vysocina Region, Moravia, in the Czech Republic. Within this geological formation, anthophyllite occurs in two distinct morphological forms: non-asbestiform and asbestiform aggregates. These anthophyllite mineral aggregates encase tightly packed sheets of phlogopite, a member of the mica group. These geological specimens are notably characterized by their nodular-like structures, wherein anthophyllite minerals completely envelop phlogopite sheets.

2.2. Sample Preparations

2.2.1. Epoxy Mount

In order to perform electron microprobe analysis (EPMA) for chemical analysis of natural tremolite and anthophyllite, a meticulous epoxy mounting technique was employed to prepare the samples. The samples were securely mounted onto a 1-inch-diameter glass disc using Buehler’s epoxy, which consisted of a weight ratio of 100 parts epoxy resin to 45 parts epoxy hardener. The sample powder was deposited onto wet epoxy, spread evenly over the surface of the mount, and allowed to dry overnight, ensuring a strong and durable bond between the sample and the glass substrate. Following the mounting process, a polishing procedure was conducted to expose the mineral grains on the smooth and even surface, facilitating comprehensive examination during subsequent electron microscopy experiments. To address the issue of electrical charging that can occur when the electron beam is directed at the sample, a thin film of conducting material (carbon coating), approximately 200 Å thick, was deposited onto the polished sample. This coating enhanced the sample’s conductivity and ensured proper charge dissipation during the EPMA measurements.

2.2.2. Ball Milling

To assess detection limits and improve the accuracy of trace-level quantification techniques, a series of six samples were prepared. These samples comprised commercial talc-based powder, a product containing mainly talc and clinocllore, mixed with various predetermined quantities of natural tremolite and anthophyllite. The bulk fibrous amphibole samples were broken down through dry milling using an oscillating mill with tungsten carbide (WC) grinding elements, operating at 30 Hz for a duration of 90 min.

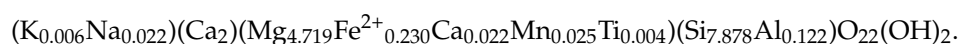
The deliberate blending process facilitated the creation of specific asbestos concentrations within the samples. The concentration targets for this study included 0.05 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, and 10 wt% natural tremolite sample and the same concentrations with natural anthophyllite sample. A WC planetary mill was employed again to assure proper mixing. A 100 mL milling jar and three 12 mm diameter WC milling balls were used, with each ball weighing 21.5 g. Additionally, 4 g of the mixed sample was placed in a WC milling jar. The ball-to-powder ratio was approximately 16:1. The milling parameters were configured with a grinding speed of 200 RPM and a total active milling time of 1 h.

2.3. Experimental Procedure

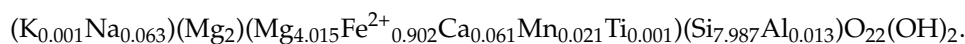
2.3.1. Electron Microprobe Analysis (EPMA)

Although both samples were found in association with other minerals, there were no available reports on the chemical composition of pure tremolite mineral and pure anthophyllite mineral from neither location. To determine the precise chemical formula of these minerals, the chemical compositions of pure tremolite and pure anthophyllite minerals were analyzed and determined using wavelength-dispersive spectrometry (WDS). The analysis was conducted at the School of Ocean and Earth Sciences and Technology, University of Hawai'i at Mānoa, using a JEOL Hyperprobe JXA-8500F electron microprobe manufactured by JEOL Ltd., Tokyo, Japan. The beam energy was set at 15 keV, with a beam current of 20 nA and a beam diameter of 2 microns.

The analysis of the only natural tremolite mineral from McIlroy Mine involved averaging the results of 40 spot analyses. This process resulted in the determination of the chemical formula for the tremolite sample.



For the natural anthophyllite mineral from Heřmanov, the analysis was conducted under comparable conditions. The chemical formula for this sample was determined based on an average of 35 spot analyses, resulting in



A set of standard minerals, including olivine, sphene, diopside, orthoclase, garnet, and albite, served as references. We determined the chemical formula by considering 23 oxygen (O) atoms, following the methodology outlined by [47] and refined by Hawthorne et al. [16]. This calculation assumes that the sum of oxygen, hydroxide (OH), fluorine (F), and chlorine (Cl) atoms equals 2 atoms per formula unit (apfu). Since no fluorine (F) or chlorine (Cl) was detected in the microprobe analysis, it was assumed that there were 2 apfu of hydroxide ions (OH). For detailed operational settings and results, please see Supplementary Materials Tables S1 and S2.

2.3.2. Powder X-ray Diffraction

We utilized a Bruker D8 Advance diffractometer equipped with a 3 kW CuK α source and a LYNXEYE XE detector at the X-Ray Atlas Diffraction Laboratory, University of Hawai'i at Mānoa. The diffractometer was manufactured by Bruker, headquartered in Billerica, Massachusetts, USA. The diffractometer operated in Bragg–Brentano parafocusing geometry, and the sample was mounted on a standard puck-type mount. The X-ray source

was operated at 40 kV and a current of 40 mA, utilizing a wavelength of 1.54060 Å. To minimize CuK α radiation, a 0.020 mm Ni filter was employed. Standard powder scans were collected over a range of 5–85 degrees, with a step size of 0.02 degrees and an exposure time of 2 s per step. For the analysis of the diffraction data, we utilized Rietveld refinement in Bruker TOPAS version 5 [48]. To achieve the best fit, the initial structures for the talc-based powder samples (talc monoclinic, talc triclinic, clinocllore monoclinic, clinocllore triclinic, and chamosite) were obtained from PDF 01-074-1036, PDF 01-073-0147, PDF 04-017-1634, PDF 01-072-1235, and PDF 04-017-1635, respectively. Similarly, the natural tremolite sample (tremolite and calcite) structures were sourced from PDF 00-020-1310 and PDF 00-005-0586, while the natural anthophyllite sample (anthophyllite, phlogopite, vermiculite, muscovite, illite, and biotite) structures were extracted from PDF 00-045-1343, PDF 00-024-0885, PDF 01-076-0847, PDF 00-0058-2036, PDF 00-0026-0911, and PDF 01-076-8343 [49]. This process involved optimizing various parameters, including background function, phase fractions, unit-cell parameters, peak profiles, site occupancies for non-oxygen atoms, and isotropic atomic displacement parameters. Once an optimal fit for the entire dataset was attained, the peak shape parameters, background parameters, and lattice parameters were fixed. In this stage, the residual Rwp, which represents the remaining differences between the observed and calculated data, provided the measure of overall fit quality [50].

2.3.3. Heavy Liquid Separation

Heavy liquids, also known as dense fluids or solutions, are utilized for the separation and concentration of materials based on their density differences. Density is the ratio of an object's mass to its volume, and materials with densities lower than that of the heavy liquid are buoyant, while those with higher densities sink. Heavy liquids are usually solutions where concentration of the solute can be adjusted to change the density to a desired value. In the context of this experiment, the focus is on the separation of amphibole asbestos minerals, which have a density greater than 2.9 g/cm³. Conversely, most of the minerals commonly present in talc-based powder exhibit densities of less than 2.78 g/cm³ (see Supplementary Materials Table S3 and Figure S1).

While conceptually simple, the heavy liquid separation method faces practical complexities due to factors such as mixed-phase grain aggregation and the entrapment of air bubbles. The buoyancy of aggregates is determined by the weighted average of all grains. These factors pose challenges to the effective implementation of the separation method. The sodium polytungstate liquid (SPT) utilized in this experiment, with a density of approximately 2.89 g/cm³, was procured from GeoLiquids, a chemical supply company. SPT was selected as an intermediary substance for this experiment due to this specific value of density falling between that of amphibole minerals and minerals found in talc-based powder. The density of SPT has been rigorously confirmed through hydrometer measurements. SPT has a light-yellow color and chemical formula Na₆[H₂W₁₂O₄₀] or 3Na₂WO₄·9WO₃·H₂O. The water solution of SPT is non-corrosive in nature, stable within a broad pH range of 2–14, and quite easy to handle. It also facilitates easy material separation based on buoyancy and can be cleaned with water, rendering it both environmentally friendly and reusable [36,51–54]. However, it is important to note the necessary safety precautions when handling tungsten. Tungsten should be used under a fume hood with appropriate personal protective equipment (PPE), such as a mask and goggles, considering its potential toxicity.

This experiment was structured into two distinct sections, with the first section being dedicated to developing an optimized protocol for the separation of mixed samples. Five different protocols were employed in this initial section. The separation process began with the crushing and ball milling of the mineral sample to achieve a finely powdered consistency, ensuring uniformity and enhancing separation efficiency. Essential laboratory equipment, including an ultrasonic homogenizer sonicator processor cell disruptor mixer with a 6 mm diameter probe, manufactured by U.S. Solid, Cleveland, OH, USA, facilitated processes such as disintegrating particle clusters and achieving sample homogenization

using high-frequency sound waves. DA-60S Vacuum Pumps, manufactured by Ulvac Sinku Kiko, Miyazaki, Japan were employed to reduce the presence of bubbles in liquid samples. The Ample Scientific Champion F-33D 15 mL Centrifuge, manufactured by Ample Scientific, Norcross, GA, USA, facilitated the separation of components within the sample. Ensuring measurement accuracy, all sample masses were meticulously determined using a 4-digit analytical balance with a precision of 0.0001 g, serving as a fundamental tool in maintaining experimental precision.

In the first protocol, 2 g of a mixed sample containing 10 wt% natural tremolite and talc-based powder was weighed and placed in a centrifuge tube. Subsequently, 10 mL of the heavy liquid solution was added, and the container was gently agitated to allow for sample dispersion. This was followed by sonication to disaggregate clusters of grains from different phases, conducted at approximately 75% intensity for 15 min in intermittent mode (5 s on, 5 s off). To minimize the formation of bubbles, a vacuum vial was utilized, and the cap of the centrifuge tube was left off for 30 min, with a maintained pumping speed of 60 L per minute at 50 Hz. The final step involved centrifugation at 1000 rpm for 30 min.

In the second protocol, 2 g of the mixed sample was weighed, and sonication with methanol was performed to disperse agglomerates, effectively minimizing the impact of temperature on SPT liquid due to methanol's low freezing point and rapid evaporation rate. After sonication (15 min at approximately 75% intensity, intermittent mode), the sample was allowed to dry before being transferred to a centrifuge tube. Subsequently, 10 mL of the heavy liquid solution was added, and the container was gently agitated to mix all materials. The final step was centrifugation at 1000 rpm for 30 min.

The third protocol was akin to the first, with the notable difference of omitting sonication. The sample (2 g of mixed 10 wt% tremolite and talc-based powder) was weighed and placed in a centrifuge tube, and 10 mL of the heavy liquid solution was added. Gentle agitation facilitated mineral equilibration. The centrifuge tube was placed inside a vacuum vial to reduce bubble formation. The cap was left off for 30 min while maintaining a pumping speed of 60 L per minute at 50 Hz. Afterward, the tube underwent centrifugation at 1000 rpm for 30 min.

The fourth protocol mirrored the second approach but incorporated the use of a vacuum vial to reduce bubble formation, with the centrifuge tube cap being left off for 30 min before centrifugation.

The fifth protocol was similar to the third, with both sonication and vacuum steps being omitted. The sample was weighed and placed in a centrifuge tube, and 10 mL of the heavy liquid solution was added, followed by gentle agitation and centrifugation at 1000 rpm for 30 min.

For all protocol designs, after centrifugation, the centrifuge tubes were left undisturbed for 24 h to allow materials to settle due to density.

Subsequently, the optimal protocol from the first section was determined for conducting experiments in the second section with varying concentrations of natural tremolite sample and natural anthophyllite sample (0.05 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, and 10 wt%) alongside talc-based powder.

In this experiment, the differential density of sodium polytungstate between tremolite and anthophyllite minerals, as well as the predominant minerals in talc-based powder, facilitated density-based material segregation. This experiment was conducted under conditions with a humidity range of 65.2–65.9% and temperatures ranging from 20.8 to 21.5 °C. Following agitation, buoyant minerals were retrieved from the container's surface, while denser minerals settled at the bottom. After settling under gravity for 24 h, liquid nitrogen was applied to freeze the material at the bottom of the centrifuge tube for a brief period, preventing further movement when pouring off the lighter material from the top. Subsequently, the concentrate of light minerals was easily poured off. Any light minerals that may have adhered to the sides of the tube could be easily rinsed out by flushing the tube with distilled water from a squeeze bottle. After the sodium polytungstate solution had been filtered through a funnel fitted with filter paper, the light mineral fraction was washed,

dried, and weighed. After the liquid nitrogen had evaporated, the bottom fraction was subsequently dried and analyzed using powder XRD to determine the phase composition of the separated materials.

3. Results

Natural tremolite and natural anthophyllite mixed with talc-based powder at various concentrations were subjected to general diffraction data evaluation using powder analysis Bruker DIFFRAC.EVA software version 4.3 [55].

A comprehensive comparative analysis of powder XRD patterns for various compositions of tremolite and talc-based powder is illustrated in Figure 1. These samples, comprising concentrations of 0.05 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, and 10 wt% tremolite, underwent rigorous high-energy milling at 200 RPM for a duration of 1 h. The utilization of XRD analysis serves as an indispensable tool for ascertaining the precise composition of these samples. Specifically, it permits the detailed examination of tremolite peaks, characterized by d values at 9.015 Å and 8.416 Å. The results from our analysis unequivocally highlight that those compositions containing tremolite concentrations ranging from trace amounts to 0.5 wt% exhibit distinct XRD peaks at both 9.015 Å and 8.416 Å, unequivocally confirming the presence of tremolite within these samples. Notably, these peaks are well defined and easily discernible. However, as the tremolite concentration decreases to 0.1 wt% and 0.05 wt%, the tremolite diffraction pattern becomes less prominent. Although diffraction peaks are still observable at 8.416 Å, their clarity diminishes, and the presence of tremolite is more challenging to ascertain at the 9.015 Å d value.

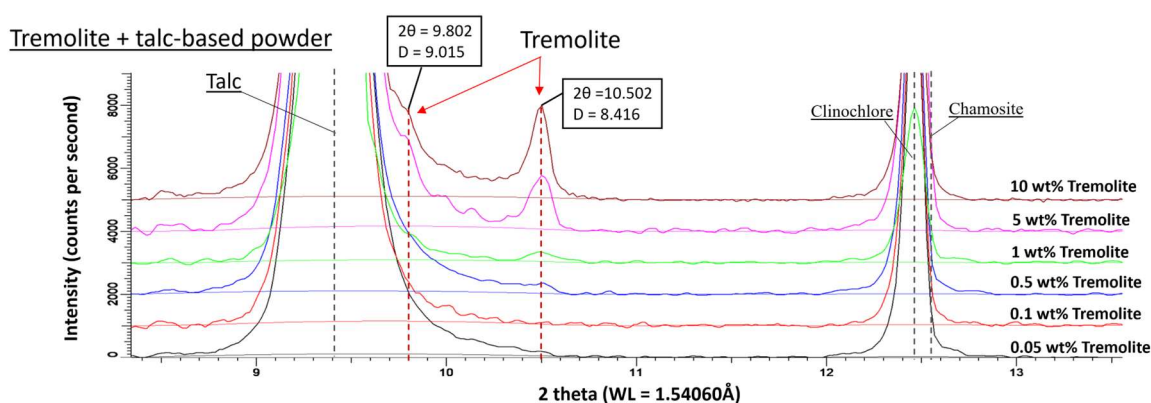


Figure 1. Powder XRD patterns for all concentrations (0.05 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, and 10 wt%) of natural tremolite sample mixed with talc-based powder. The red dotted line and red arrows indicate the tremolite diffraction peaks.

Similarly, in Figure 2, we embarked on a comparative examination of powder XRD patterns elucidating various compositions of anthophyllite and talc-based powder, at concentrations of 0.05 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, and 10 wt%. This analytical approach allows us to discern the presence of anthophyllite through the identification of characteristic peaks with d values situated at 8.977 Å and 8.224 Å. Our findings unequivocally establish that the composition containing 10 wt%, 5 wt%, 1 wt%, and 0.5 wt% anthophyllite exhibits well-defined XRD peaks at both 8.977 Å and 8.224 Å, thereby substantiating the unequivocal presence of anthophyllite within this particular sample. However, similar to the observations made with tremolite, when investigating compositions comprising 0.1% and 0.05% natural anthophyllite blended with talc-based powder, the diffraction pattern indicative of anthophyllite becomes less conspicuous. Although diffraction peaks endure at 8.224 Å, their resolution diminishes, rendering the identification of anthophyllite at 8.977 Å more challenging.

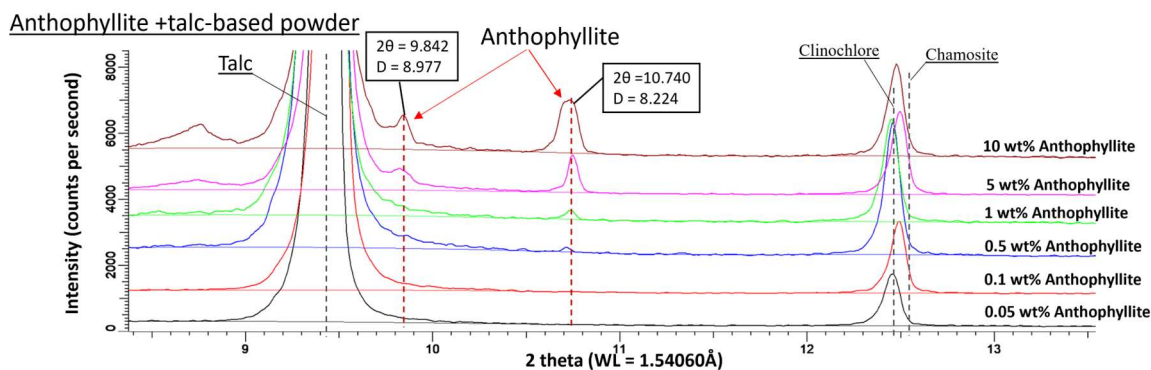


Figure 2. Powder XRD patterns for all concentrations (0.05 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, and 10 wt%) of natural anthophyllite sample mixed with talc-based powder. The red dotted line and red arrows indicate the tremolite diffraction peaks.

The identification and quantification of tremolite and anthophyllite become less sensitive when their concentrations drop below 0.5 wt%. To address this limitation and enhance analytical sensitivity, heavy liquid separation techniques were employed. These techniques are designed to improve sensitivity by eliminating non-target materials from the sample matrix, particularly those that could interfere with the detection of the target analytes.

In the first section of heavy liquid separation, five different methods were investigated. Among these methods, the fifth approach emerged as the most effective protocol for separating tremolite fibers from talc-based powder, as evidenced by its minimal weight loss. When starting with a 2 g mixture of 10 wt% tremolite and talc-based powder sample (calculated from the XRD experiment, indicating that the mixed sample comprises 0.2 g of natural tremolite and only 0.14 g of pure tremolite), the weight of the remaining material after the experiment was 0.1120 g for the fifth method. In contrast, the second method left 0.096 g; the third method left 0.1080 g; and the fourth method left 0.0779 g of material. It is worth noting that the first method was ineffective in separating the minerals because the sodium polytungstate (SPT) solution solidified after sonication due to the temperature effect. These results are summarized in Table 1 and shown in Figure 3.

Table 1. First section experiment of heavy liquid separation of mixed 10 wt% natural tremolite and talc-based powder using SPT with a density of 2.89 g/cm³ as the intermediate liquid.

Method No.	Process	Sink Material Weight after HL (g)
1	Mixed samples + SPT + sonication + vacuum + centrifugation	Cannot calculate
2	Mixed samples + sonication with methanal + SPT + vacuum + centrifugation	0.0959
3	Mixed samples + sonication with methanal + SPT + vacuum + centrifugation	0.1080
4	Mixed samples + sonication with methanal + SPT + vacuum + centrifugation	0.0779
5	Mixed samples + sonication with methanal + SPT + vacuum + centrifugation	0.1120

In the initial phase of our study, Method No. 5 emerged as the optimal approach for this experiment. Subsequently, we applied this protocol to samples featuring varying concentrations of tremolite and anthophyllite (0.05 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, and 10 wt%) mixed with talc-based powder in the second section of the heavy liquid separation experiment. The outcomes unequivocally confirmed the success of the separation process. Minerals within the mixed samples, with a density lower than 2.89 g/cm³, particularly those resembling the majority of minerals present in talc-based powder and the common mica mineral group often found in conjunction with natural

anthophyllite, exhibited buoyancy, causing them to float to the surface. In contrast, minerals with a density exceeding 2.89 g/cm^3 sank to the bottom (Figures 4 and 5).

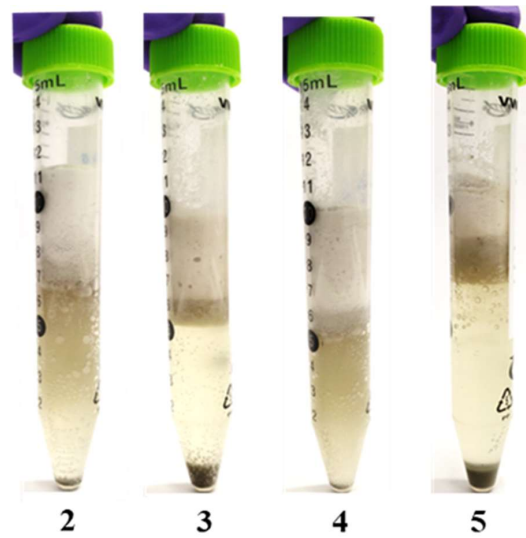


Figure 3. Centrifuge tubes of mixed 10 wt% tremolite with talc-based powder were left undisturbed for 24 h. Each centrifuge tube was labeled with a method number corresponding to the separation of tremolite fibers from talc-based powder in the second, third, fourth, and fifth methods. The first method was ineffective as the SPT solution solidified post-sonication due to temperature effects.

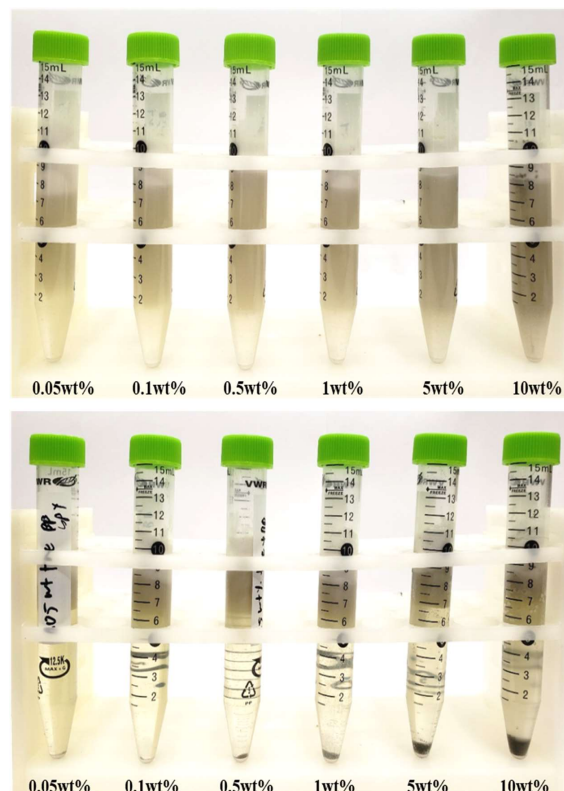


Figure 4. This image illustrates mixed samples at various concentrations of tremolite with talc-based powder in the presence of sodium polytungstate liquid. Each centrifuge tube is labeled with the corresponding wt% concentration of tremolite with talc-based powder. The top image reflects the state after centrifugation, while the bottom image represents the condition after 24 h of settling.

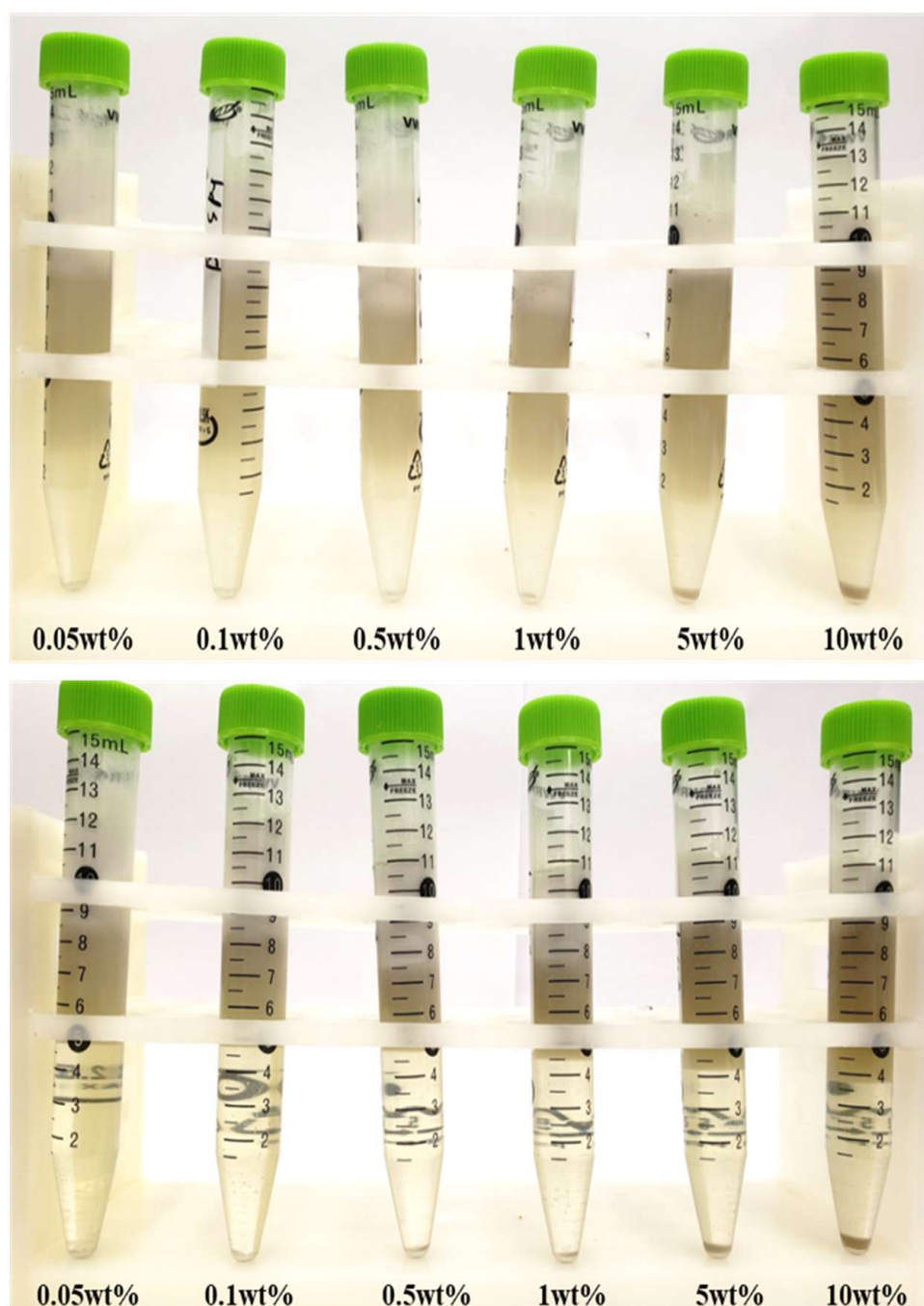


Figure 5. This image illustrates mixed samples of various concentrations of anthophyllite with talc-based powder in the presence of sodium polytungstate liquid. Each centrifuge tube is labeled with the corresponding wt% concentration of anthophyllite with talc-based powder. The top image reflects the state after centrifugation, while the bottom image represents the condition after 24 h of settling.

The sink material fraction underwent analysis using powder XRD. The results clearly demonstrate the effective removal of non-target materials from the sample matrix, thereby enhancing the diffraction peaks of the target analytes, in this case, pure tremolite and pure anthophyllite (Figures 6 and 7). Notably, even at concentrations as low as 0.1 wt% and 0.05 wt%, well below the 0.5 wt% threshold, diffraction patterns of tremolite and anthophyllite were successfully detected (Figures 8 and 9). This underscores the robustness of our methodology in discerning trace concentrations of these target minerals.

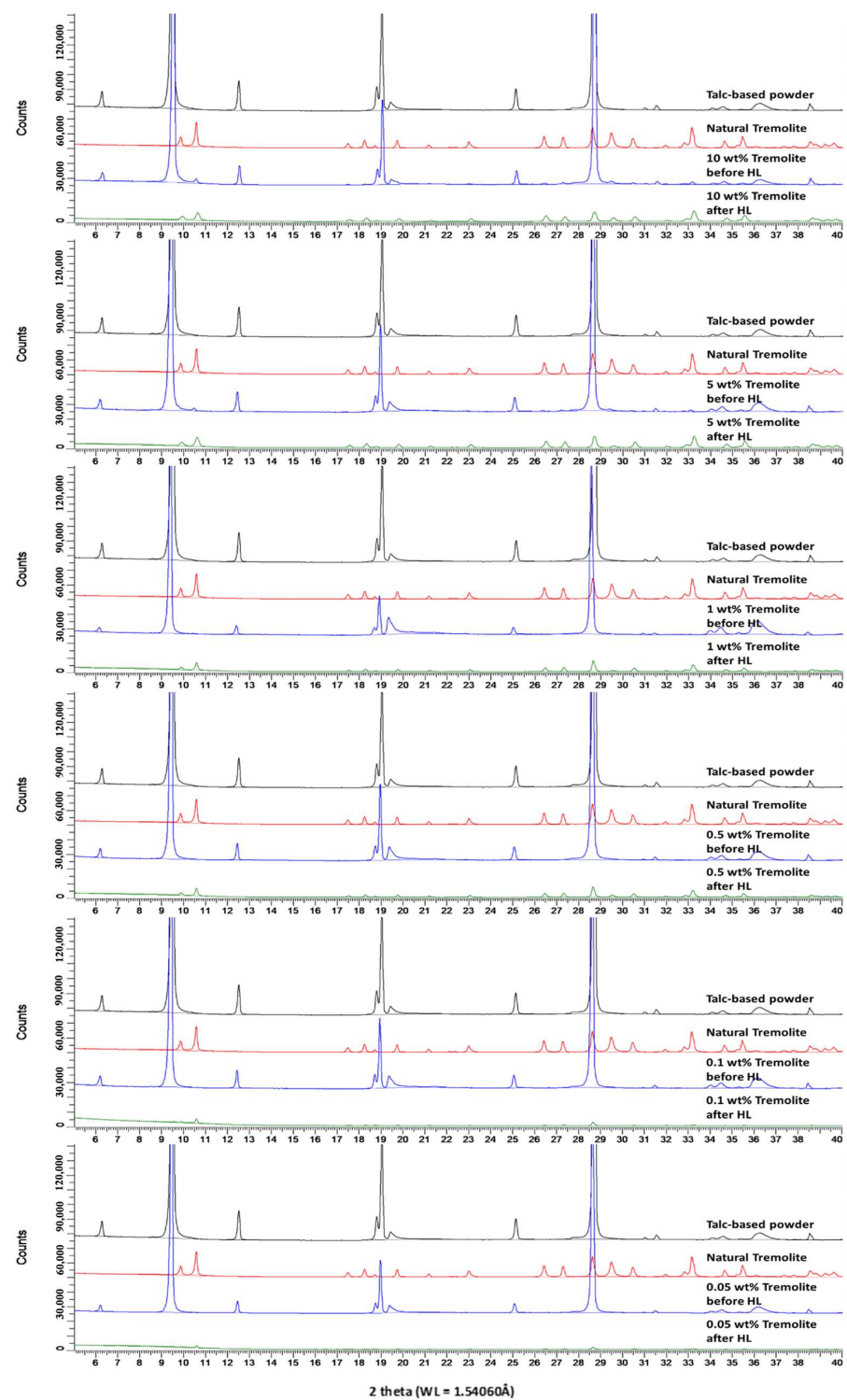


Figure 6. The XRD patterns for various concentrations of natural tremolite mixed with talc-based powder. The back line corresponds to the diffraction pattern of talc-based powder. The red line represents the diffraction pattern of natural tremolite. The blue line represents the diffraction pattern of mixed tremolite at different concentrations prior to heavy liquid separation, while the green line represents the diffraction pattern of the sink material for each concentration after undergoing the heavy liquid separation process.

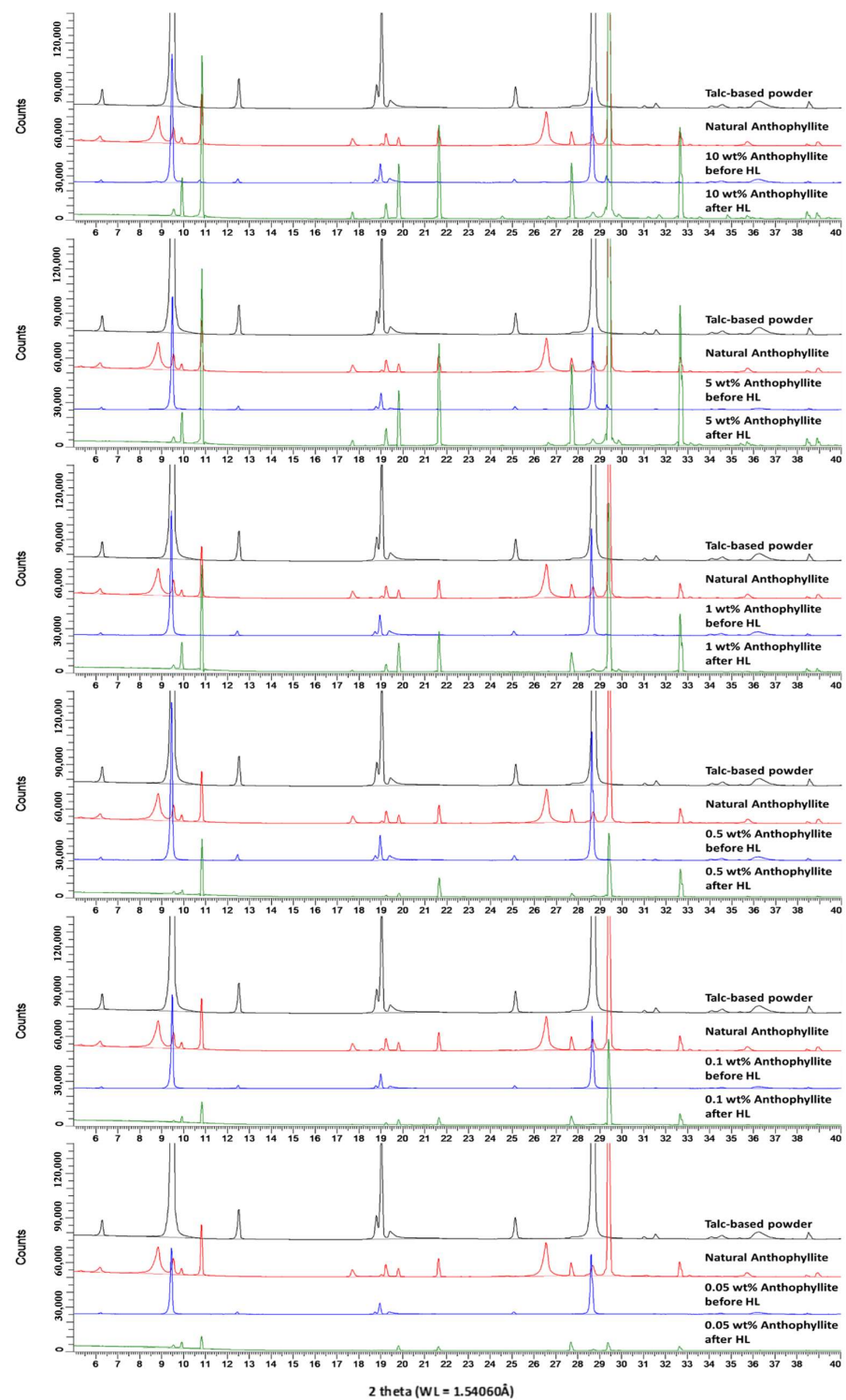
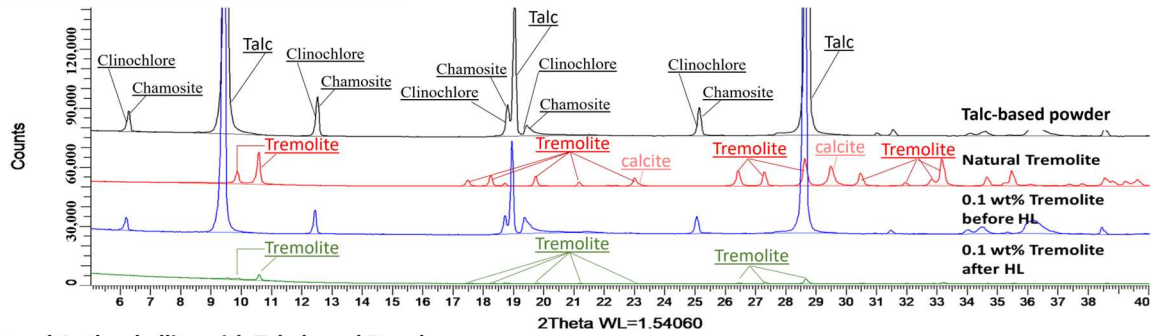


Figure 7. The XRD patterns for various concentrations of natural anthophyllite mixed with talc-based powder. The back line corresponds to the diffraction pattern of talc-based powder. The red line represents the diffraction pattern of natural tremolite. The blue line represents the diffraction pattern of mixed tremolite at different concentrations prior to heavy liquid separation, while the green line represents the diffraction pattern of the sink material for each concentration after undergoing the heavy liquid separation process.

(a) Natural Tremolite with Talc-based Powder



(b) Natural Anthophyllite with Talc-based Powder

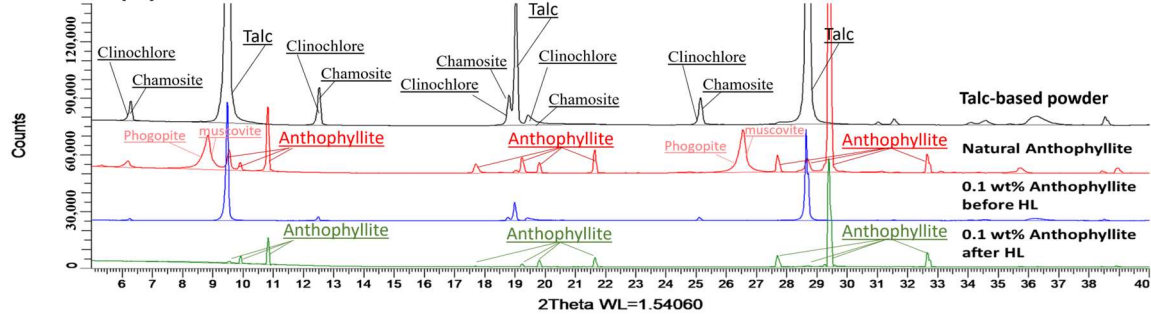
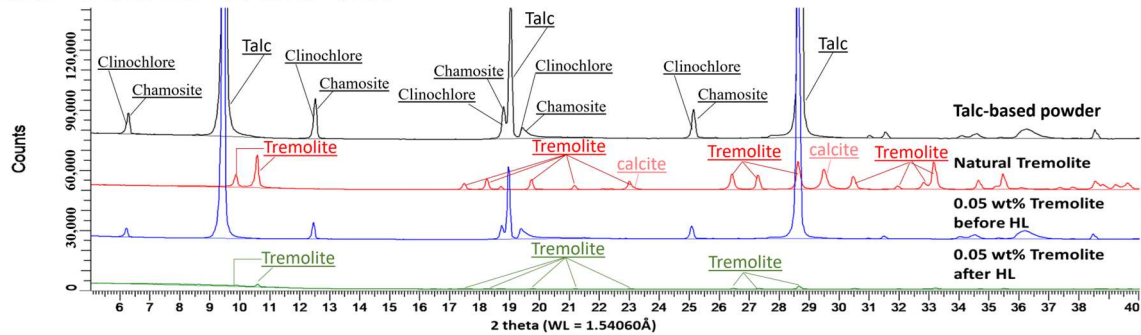


Figure 8. The XRD patterns for 0.1 wt% natural tremolite (a) and anthophyllite (b) mixed with talc-based powder and the mineral identification. The diffraction patterns of tremolite and anthophyllite, represented by the green line, were distinctly detected. This line signifies the diffraction pattern of the sink material for each concentration after undergoing the heavy liquid separation process.

(a) Natural Tremolite with Talc-based Powder



(b) Natural Anthophyllite with Talc-based Powder

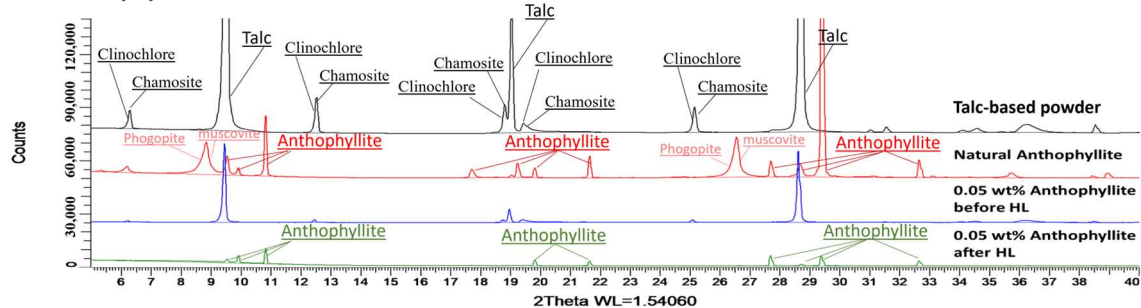


Figure 9. The XRD patterns for 0.05 wt% natural tremolite (a) and anthophyllite (b) mixed with talc-based powder and the mineral identification. The diffraction patterns of tremolite and anthophyllite, represented by the green line, were distinctly detected. This line signifies the diffraction pattern of the sink material for each concentration after undergoing the heavy liquid separation process.

The weight measurements of tremolite and anthophyllite before and after the heavy liquid separation experiment are summarized in Table 2. Notably, tremolite exhibited less weight loss than anthophyllite in this experiment. To address uncertainty, heavy liquid separation was reproduced on the mixed anthophyllite sample. Upon examination, the weight loss in the reproduced experiment for anthophyllite was found to be less than in the initial experiment of the mixed anthophyllite sample. The relationship of weight loss during separation is elucidated in Figure 10.

Table 2. The weight measurements of pure tremolite and pure anthophyllite at all concentrations, both before and after the implementation of heavy liquid separation using SPT at a density of 2.89 g/cm³, are provided. The separation protocol employed in this table is derived from Protocol No. 5.

Pure Tremolite				Pure Anthophyllite					
						Reproduced			
Wt%	Before (g)	After (g)	Weight Loss (%)	Wt%	Before (g)	After (g)	Weight Loss (%)	After (g)	Weight Loss (%)
10	0.1400	0.0918	34.40	10	0.1200	0.0911	24.11	0.0844	29.69
5	0.0700	0.0635	9.28	5	0.0600	0.0259	56.83	0.0418	30.30
1	0.0140	0.0114	18.29	1	0.0120	0.0076	37.00	0.0118	1.50
0.5	0.0070	0.0065	7.43	0.5	0.0060	0.0049	18.33	0.0059	2.00
0.1	0.0014	0.0013	8.57	0.1	0.0012	0.0009	24.17	0.0008	30.00
0.05	0.0007	0.0006	8.57	0.05	0.0006	0.0005	6.67	0.0005	20.00

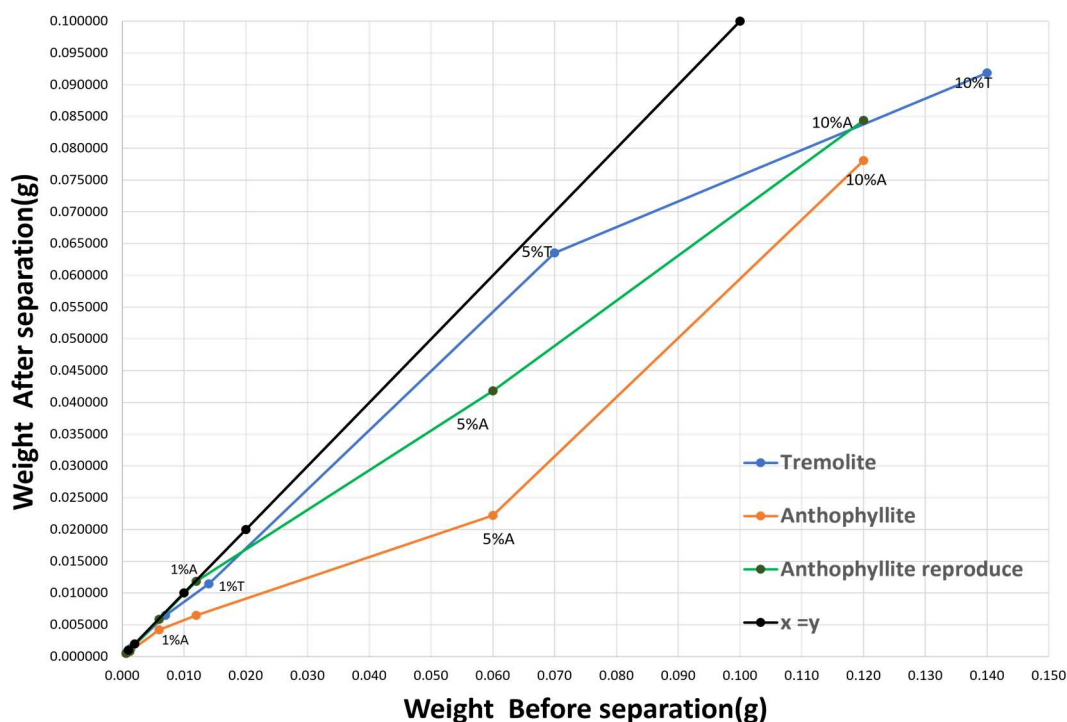


Figure 10. The relationships of weight before and after during the separation process across all concentrations of pure tremolite and pure anthophyllite.

4. Discussion

The results gleaned from this research experiment unequivocally establish that the limit of detection for powder XRD in trace-amount samples stands at approximately 0.5% by weight. Detecting target materials with concentrations lower than 0.5% becomes an arduous endeavor. The observed alignment with Block’s 2014 study [20] and correlation with Cosmetic, Toiletry, and Fragrance Association’s (CTFA) method J4-1 [21] enhance

the reliability of this established threshold. Detecting materials below this limit presents significant challenges, emphasizing the practical implications for analytical precision in both scientific and industrial applications.

However, the heavy liquid separation technique proves invaluable in eliminating non-target materials present in the sample matrix. In this particular case, the majority of minerals found in talc-based powder and the natural minerals occurring alongside tremolite and anthophyllite minerals pose as non-target materials that may interfere with the detection of the target analyte, tremolite, and anthophyllite.

For the initial phase of heavy liquid separation, five distinct methods were devised to ascertain the most efficacious protocol in this experimental context. The methods encompassed the use of sonication, vacuum, and centrifugation. While sonication primarily affects the physical and mechanical attributes of the sample, it can indirectly influence temperature during the experiment. Protocol Design No. 1 provides compelling evidence that sonication exerts an influence on the state of the separatory funnel (SPT) liquid. The SPT solution can undergo a complete transformation into a solid, albeit a reversible one, but this is not conducive to the experiment's workflow. Consequently, it is imperative to be cognizant of these effects and take necessary precautions to uphold the desired experimental conditions, especially when dealing with temperature-sensitive materials or reactions. Furthermore, there exists a potential for slight sample loss during sonication. While this technique proves effective in disassembling aggregates and ensuring uniform particle distribution, there remains a slight probability of sample loss owing to factors such as splashing or aerosol formation, particularly when dealing with minute quantities of material.

When mixing or agitating a sample, especially if it contains a liquid component, physical agitation may induce the formation of bubbles. These bubbles emerge as a result of entrained gas, usually air, within the liquid or the dispersion of gas-containing pockets within the sample. Vacuum degassing serves as a method to mitigate or eradicate these bubbles by eliminating dissolved gases from the liquid. Although, in the context of this experiment, there appears to be a minimal disparity in weight loss results between the usage of a vacuum (Protocol No. 3) and its omission (Protocol No. 5), it remains important to note that employing a vacuum to reduce bubbles can indeed prove effective, albeit with a potential risk of sample loss if not executed carefully.

Monitoring weight loss is a form of quality control. Consistent weight loss in replicate experiments indicates reproducibility and reliability of the separation method. Blount [23] used solutions such as Klein's solution (cadmium borotungstate) or Clerici's solution (thallium formate-malonate), both with a specific density of 2.81 g/cm^3 , to suspend talc containing 0.06–1% tremolite. When comparing this method to the more typical method that does not remove interfering minerals, Blount concluded that the centrifugal concentration method yielded similar results and provided approximately the same recovery when considering particle aspect ratio. The recovery and detection of tremolite at the 0.06% level were around 70%, while at higher tremolite levels, they were approximately 90%. Blount's research results align with the findings of this experiment, wherein we successfully recovered and detected tremolite at approximately 65% at the lower level and about 90% at higher levels. It is crucial to note that tremolite in its natural state can occur in both asbestiform and non-asbestiform forms, potentially posing challenges to its separation from talc, particularly when compared with equant-shaped cleavage fragments. Regarding anthophyllite, we observed higher weight loss compared with tremolite. This discrepancy may be attributed to the variability in iron content and solid solution with other amphiboles, presenting a distinct challenge. Some iron-rich anthophyllite, denser than the SPT (2.89 g/cm^3) used in this experiment, sinks, while other forms with lower density may float. Relying solely on SPT for anthophyllite separation may prove insufficient. Despite observing more weight loss in anthophyllite during the initial experiment, we were still able to recover and detect anthophyllite at approximately 70% at the lower level and 95% at higher levels in the reproduction experiment.

The higher loss rates observed in the larger weight % masses of asbestos samples (10% and 5%) compared with the smaller weight % masses in the heavy liquid separation experiment may be attributed to several factors. One potential reason could be the influence of increased sample mass on the effectiveness of the separation process. As the mass of asbestos in the sample increases, there may be greater challenges to achieving uniform and efficient separation, leading to higher losses. Additionally, variations in the distribution and composition of minerals within larger weight % masses could contribute to increased complexities in the separation process, affecting the overall recovery rates. Further investigation and experimentation with a focus on optimizing the separation conditions for larger sample masses may provide insights into mitigating these higher loss rates.

This research underscores the feasibility and practicality of separating tremolite and anthophyllite particles from substances like talc-based powder through centrifugation in a heavy liquid. It is evident that this method has the potential to be effective in isolating these mineral phases. However, it is crucial to acknowledge that the widespread adoption of the heavy liquid separation (HLS) technique for the quantitative isolation of trace asbestos levels necessitates further investigation into its reproducibility and accuracy.

To enhance the efficacy of asbestos analysis, future studies should focus on the development of more advanced and sensitive analytical methods. These refinements will be instrumental in ensuring that the HLS technique can consistently and accurately detect and quantify low levels of asbestos in various samples. By addressing these research needs, we can continue to improve our ability to assess and manage potential health risks associated with asbestos-containing materials in the environment.

5. Conclusions

In summary, our study involved the analysis of natural tremolite and natural anthophyllite mixed with talc-based powder at various concentrations using powder analysis. We conducted a comprehensive comparative analysis of powder XRD patterns for different compositions of tremolite and talc-based powder, as well as anthophyllite and talc-based powder. The XRD analysis allowed us to identify the presence of tremolite and anthophyllite in the samples based on characteristic diffraction peaks.

To enhance sensitivity, we employed heavy liquid separation techniques in the first section, with the fifth method protocol proving the most effective for separating the target analytes (i.e., tremolite) from talc-based powder. Subsequently, we applied this optimal protocol to samples with varying tremolite and anthophyllite concentrations mixed with talc-based powder. The results confirmed successful separation based on density differences. Minerals with densities below 2.89 g/cm^3 , similar to the densities found in talc-based powder and common mica minerals, floated to the surface, while denser minerals sank to the bottom.

Powder XRD analysis of the sink material fraction demonstrated the removal of non-target materials, enhancing the diffraction peaks of pure tremolite and anthophyllite. Tremolite exhibited lower weight loss than anthophyllite when using sodium polytungstate liquid at 2.89 g/cm^3 as an intermediate liquid. Separating tremolite and anthophyllite from talc through centrifugation in a heavy liquid is theoretically possible and also a practical technique.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst14020127/s1>, Table S1: EPMA analytical setup and standards, Table S2: Chemical analyses for pure tremolite and pure anthophyllite from EPMA, Table S3: Mineral composition of starter materials and their density, Figure S1: The density of the minerals found in the samples used for this experiment.

Author Contributions: Conceptualization, S.C. and P.D.; methodology, S.C., P.Q.H.N., and P.D.; software, P.D.; validation, P.D.; formal analysis, S.C.; investigation, S.C.; resources, P.D.; data curation, S.C.; writing—original draft preparation, S.C.; writing—review and editing, S.C., P.D., P.Q.H.N., and R.T.D.; supervision, P.D. All authors have read and agreed to the published version of the manuscript.

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